

EFFECT OF THERMAL AND CHEMICAL PRETREATMENTS ON THE COPPER-CATALYZED GASIFICATION OF CARBON IN AIR

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INTRODUCTION

Copper is one of the most active catalysts for the gasification of carbon in oxygen [1]. Its high activity is thought to be related to the ease with which copper can undergo oxidation/reduction cycles at gasification conditions [2-6], thereby promoting the transfer of oxygen atoms to the (re)active carbon sites [2,7]. Evidently, oxygen transfer rates will be faster for smaller catalyst particles, which provide a higher degree of catalyst-carbon interface contact. (This explains the observed structure-sensitivity of the Cu- (and other metal-) catalyzed carbon gasification in air [8,9].) However, smaller particles are also more susceptible to catalyst-support interactions [10]. In this report we examine the role of carbon surface chemistry in (a) securing a high and thermally resistant Cu dispersion; and (b) affecting the kinetics of the Cu-catalyzed gasification process.

EXPERIMENTAL

For brevity this report will concentrate on the gasification of a highly pure, polymer-derived microporous carbon (Saran, Dow). Results on other (less porous or non-porous) carbons will be addressed at length elsewhere [11]. All carbons were subjected to a wide variety of thermal and/or chemical treatments aimed at modifying their surface properties (see Ref. 12). Changes in the surface chemistry and physics of the carbons were followed by techniques such as acid/base and mass titrations [12], electrophoresis [12,13], temperature-programmed desorption [14], N_2 and CO_2 adsorption [15], XPS [9], XRD [7,15] and others [11]. Selected samples were impregnated with copper acetate (Fisher) by incipient wetness or ion exchange (without filtering) to yield 5% Cu catalysts (dry carbon basis). In the latter case, the exchange on selected carbons was monitored by withdrawing small aliquots of supernatant after partial equilibration (ca. 30 min) and measuring the copper concentration remaining in solution with an ion-selective electrode (Orion). Gasification reactivities of all catalysts in 0.1 MPa air were measured on a modified TGA-7 apparatus (Perkin-Elmer) under conditions of chemical reaction control [9,14].

RESULTS AND DISCUSSION

Adding copper to Saran (and other) carbons was found to increase their maximum gasification rate in air by 2-3 orders of magnitude. (The method of Cu addition is important, since physically mixed Cu acetate was found to enhance the rate only by a factor of ca. 30.) It was also noted that both chemical and thermal treatments of the carbons alone affect their uncatalyzed reactivities, but only to well within the same order of magnitude [11]. Hence, the importance of chemical and thermal treatments lies in their effect on the distribution (dispersion) of the active catalyst phase throughout the carbon substrate [7]. In general, chemical treatments can be used to increase the dispersion of copper, and thermal treatments tend to decrease it. The contribution by these seemingly opposing effects to carbon gasification by Cu will be addressed below.

Copper Adsorption on Carbon. Anchoring metal precursors onto carbon by adsorption is thought to be necessary in order to attain the highest possible metal dispersion [13]. Copper acetate dissociates in dilute aqueous solutions to yield mainly hydrated Cu^{+2} ions; these ions are stable below pH=6, and precipitate as hydroxide at high pH unless they are complexed by, e.g., NH_3 , in which case they form a pH-dependent mixture of $[Cu(NH_3)_n(H_2O)_{6-n}]^{+2}$ ammine complexes ($1 \leq n \leq 5$) [16]. On the other hand, carbon surfaces can be pretreated to contain various kinds and amounts of surface functional groups [11-13] which differ in their chemical and thermal properties. For instance, low-temperature

oxidative treatments produce a mixture of strongly and weakly acidic oxygen complexes (discernible by neutralization with bases of increasing strength [11,14,15]) which decompose upon TPD according to their thermal strength to yield primarily CO_2 and CO (see Table 1) at relatively low and high temperatures, respectively. Increasing the pH of a carbon slurry leads to an increase in the number of dissociated, negatively charged functional groups, which can then act as anchors for metal cations [13]. Consequently, it was confirmed that the uptake of copper by carbon increases with increasing pH in the range $2.5 \leq \text{pH} \leq 11.5$ [11]. Figure 1 shows the adsorption isotherms of copper on selected pretreated carbons (see Table 1) at $\text{pH} = 11.5$. Relative to the untreated sample (CU), it is seen that the removal of oxygen functionalities by heat pretreatment (sample CH) lowers the copper adsorption capacity, while the introduction of functional groups by mild preoxidation (samples CA and CN) increases it.

The role of functional group dissociation in promoting metal ion sorption on carbon can be conveniently illustrated using electrophoretic mobility (EM) diagrams [13]. Figure 2 shows a typical EM diagram for a microporous, mildly oxidized carbon. It is shown that the pH of zero mobility, IEP (above which the net external surface charge of the carbon is negative), is over one pH unit lower than the point of zero net surface charge, PZC (determined by mass titration). This is taken as an indication that typical oxidative treatments or subsequent air exposure of microporous carbons leads to an inhomogeneous surface charge distribution, with the external (geometric) surface being enriched in negatively charged groups when $\text{IEP} < \text{PZC}$ [13-15]. Hence, the observed increase in reactivity with increasing pH (Figure 2) can be attributed to an increase in the sorption of the Cu precursor leading to a higher catalyst dispersion. Figure 2 shows a maximum (and only three times higher) reactivity at $\text{pH} = 8.5$. Since the 5% Cu/C catalysts used to generate Figure 2 were made by ion exchange without filtering, the nonadsorbed copper probably forms larger, less active catalyst particles when the dried Cu/C samples are preheated to reaction conditions. However, the large surface area and the microporosity of these materials [12] preclude an extensive agglomeration and growth of copper particles [15], i.e., an extreme loss in reactivity. This is in agreement with XPS experiments, which indicate an external surface enrichment in Cu particles [9], particularly after heat treatment. The apparent maximum reactivity, also observed for samples prepared by incipient wetness using solutions of preadjusted pH [11], can arise from two factors. First, upon drying to remove the excess solvent, the concentration of ions (e.g., OH^- , Cu amines) remaining occluded increases, thereby forcing further adsorption to take place in order to regain equilibrium. Since competition for sorption sites by NH_4^{+1} can be neglected, especially above $\text{pH} = 9.25$ [16], a maximum copper adsorption in the pH range 9-10 is to be expected [17]; above $\text{pH} = 10$ the contribution by hydroxides becomes measurable [16], and their precipitation facilitates Cu agglomeration upon heating. Second, the adsorption mechanisms of the predominant Cu species at different pH values may differ [18]. Attempts to desorb Cu from portions of dried (in vacuum at 313 K) batches ion exchanged at $\text{pH} = 8.5$, by washing with distilled water, failed. However, traces of copper could be desorbed from the samples prepared at $\text{pH} = 11.5$. In both cases, the strong adsorption suggests that some ligand exchange may have taken place. However, the exchange sites at both pH values differ; at $\text{pH} = 11.5$, more weakly acidic sites are activated for copper adsorption, but since the carbon surface becomes more negatively charged, the density of positive ions held electrostatically around these negative charges increases. (This effect is accompanied by the shrinkage of the diffuse portion of a hypothetical "double layer" surrounding the carbon surface [19].) The net result is the saturation of the carbon surface with positive charges which must repel each other and hence limit the access of the desired adsorbing cations to some negatively charged surface sites. Table 1 includes the estimated adsorption ratios of Cu to CO_2 -evolving and to total acidic (NaOH-titratable) surface groups. The role of individual surface functional groups in promoting Cu dispersion and reactivity is addressed in detail in an accompanying paper [20].

Copper Dispersion on Carbon. The growth in average Cu crystallite diameter (measured by XRD) with heat pretreatment temperature is best illustrated in Figure 3. In all cases, heating the freshly prepared Cu/C catalysts in inert flowing gas (N_2) leads to Cu crystallite growth. Whereas the growth of Cu crystallites in samples CU and CH is comparable, that on sample CN is much less pronounced, despite the latter's lower surface area [12]. Since the main difference between samples CU and CH is the higher CO evolution yield of sample CU (Table 1), it follows that CO -evolving groups do not contribute directly to the adsorption or subsequent dispersion of Cu cations. (In contrast, PtCl_6^{2-} [21] and $\text{HMo}_2\text{O}_7^{-1}$ [10] anion adsorption and subsequent metal dispersion were reported to be enhanced by the presence of CO -evolving groups.) On the other hand, CO_2 -evolving groups appear to correlate better with copper adsorption. The amount of CO_2 evolved upon TPD is believed to be related to the

number of carboxyl-type ($-\text{COO}^-$) groups present on a carbon surface, with one (plus one CO) or two CO_2 molecules being desorbed from two adjacent [21] or distant [21,22] carboxyl functionalities, respectively. Indeed, for the calcium carbon system ($\text{Ca}^{+2}/\text{CO}_2$ ratios of 0.5-1.25 have been taken as an indication that each cation adsorbs onto two negatively charged carboxyl groups [21]. In our case, Cu/CO_2 ratios of 0.32-0.87 (Table 1) could also be interpreted along these lines. However, since NaHCO_3 is believed to selectively neutralize the carboxyl groups on a 1:1 ratio [23], the poor agreement between Cu and NaHCO_3 uptakes (Table 1) suggests that in addition to carboxyl groups there are other (non CO -desorbable) surface groups which also participate in the copper adsorption process. Evidence in favour of the obvious choice, i.e., lactones [23], is presented in an accompanying report [20].

Gasification Reactivity of Cu/C Catalysts. Broadly speaking, the surface chemistry of carbons is related to their oxygen content [22], which can be adjusted by subjecting the carbons to selected chemical pretreatments [12]. Figure 4 shows the influence of the oxygen content of chemically pretreated Saran carbons on the gasification reactivity of the Cu/C catalysts (extrapolated when necessary to 623 K), after subjecting the catalysts to selected heat pretreatments. Following low temperature (623 K) heat pretreatments, a maximum reactivity is observed at intermediate oxygen contents. This is consistent with the observation that moderate (i.e., neither too mild nor too severe) oxidative pretreatments are most successful in producing homogeneously charged ($\text{IEP} = \text{PZC}$) carbon surfaces [12], because even though sample CA adsorbs less copper than, e.g., sample CN (Table 1), its adsorbed copper is more uniformly distributed (i.e., internally as well as externally) throughout each carbon particle. However, the resistance to Cu agglomeration over the surface of sample CA is inadequate and hence sample CA experiences a more severe loss of reactivity compared to all other samples (Figure 5). For all samples the normalized reactivity (at 623 K) is most severely affected by heat treatments in the range 623-923 K (Figure 5). TPD experiments indicate that the primary effect of heat pretreatments of the carbons alone in the temperature range 623-923 K is the desorption of CO_2 -evolving (e.g., carboxyl and lactone) surface groups [12,22]. Hence the introduction (by chemical pretreatment) of CO_2 -evolving groups prior to copper adsorption enhances not only the Cu dispersion but also the gasification reactivity of the carbon.

Figure 5 also shows that the removal of further (mainly CO -evolving) surface groups via heat pretreatments in the range 923-1223 K has less bearing on the magnitude of the loss of gasification reactivity. Nonetheless, Figure 4 suggests that the remaining (CO -evolving) groups do play a role in enhancing the magnitude of the reactivity. Since these groups are not likely to act as metal precursor adsorption sites, their role in securing a higher reactivity can be explained by recalling that the thermally stable groups remaining after each heat treatment can act as diffusion barriers to the agglomeration of Cu particles [24], in which case the higher reactivities of carbons with higher initial oxygen contents can be ascribed to their higher Cu dispersion after heat treatment.

The kinetics of the gasification process are also affected by both chemical and thermal pretreatments. Figure 6 shows that for all carbons thermal treatments of Cu/C catalysts increase the apparent activation energies (E_{ACT}) of the reaction. (An analogous behaviour is observed when using nonporous carbon black substrates [11].) The increase is more significant for the samples with the highest initial oxygen content. Samples with the lowest initial oxygen content yield E_{ACT} values approaching those of the high-temperature (1223 K) heat treated catalysts, thereby suggesting that the decrease in E_{ACT} values is related to the initial oxygen content of the carbons. Therefore, in addition to enhancing the dispersion of Cu by serving as diffusion barriers to its migration, thermally stable carbon-oxygen complexes can also be more difficult to gasify than reactive intermediates [25]. If so, oxygen-rich samples would readily yield highly dispersed catalyst particles upon thermal loss of the unstable Cu anchors, but their catalytic activity would be less temperature-sensitive than that of similar catalysts on oxygen-lean carbons, whose edges would be more susceptible to the exothermic formation of readily desorbable intermediates. This interpretation is consistent with (a) an apparent compensation effect observed for the catalysts heat treated to low temperatures [9,11], (b) the faster deactivation of (initially) oxygen-rich samples [11], and (c) a higher oxygen partial pressure dependence for the gasification of Cu/C samples with the least initial oxygen content [11].

CONCLUSIONS

Both chemical and thermal treatments play a crucial role in determining the gasification behaviour of Cu/C catalysts. Chemical pretreatments can be applied in order to enhance the concentration of CO₂-desorbable surface groups, which promote copper adsorption, catalyst dispersion, and Cu/C gasification reactivity. Thermal treatments lead to the agglomeration (and consequent reactivity loss) of the catalyst, particularly for carbons with low initial oxygen content. In both cases, the effects can be related to the influence of surface oxygen complexes on the reaction. Thermally unstable (moderately to strongly acidic, e.g., carboxyl and lactone) oxygen functional groups can favour gasification reactivity by acting as desorbable anchors for metal precursors. On the other hand, thermally stable groups appear to serve both as diffusion barriers to metal agglomeration (a desirable effect) and as stable reaction intermediates which are less readily gasified by the catalyst (an undesirable effect).

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Table 1. Features of Some Chemically Modified Saran Carbons Used as Cu Catalyst Supports.

Sample ^a	%O	TPD [mmol/g] ^b		SN [mmol/g] ^b		Cu ads. ^c [mmol/g]	Cu/CO ₂ [mol/mol]	Cu/NaOH [mol/mol]
	(wt.)	CO ₂	CO	NaHCO ₃	NaOH			
CH	0.8	0.09	0.30	0.01	0.09	0.03	0.36	0.37
CU	1.6	0.12	0.74	0.01	0.11	0.04	0.34	0.36
CP	5.6	0.91	1.69	0.35	2.07	---	---	---
CA	12.0	1.03	5.42	0.81	2.70	0.90	0.87	0.34
CN	20.8	4.11	4.78	0.58	2.03	1.26	0.32	0.62

^a Pretreatments: CH, heat-treated in N₂ at 1223 K; CU, untreated; CP, oxidized in H₂O₂ at 373 K; CA, oxidized in air at 673 K (25% burnoff); CN, oxidized in HNO₃ at 363 K.

^b TPD: Temperature Programmed Desorption; SN: Selective Neutralization (with bases).

^c Amount of copper withdrawn from solution at pH=11.5 (adjusted using NH₄OH).

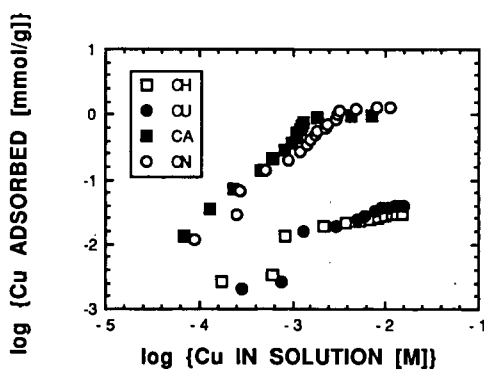


Figure 1. Influence of Chemical Pretreatment on the Adsorption of Copper by Saran Carbons (pH=11.5).

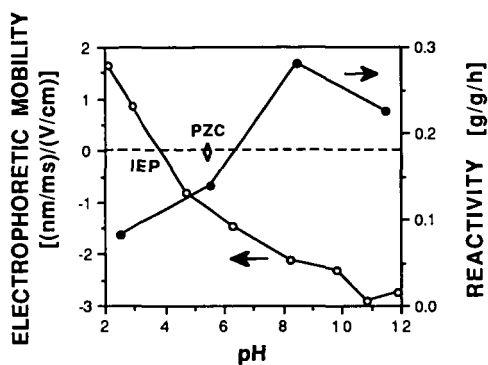


Figure 2. Relevance of Carbon Surface Charge to its Copper-Catalyzed Gasification Reactivity (at 573 K) in 0.1 MPa Air.

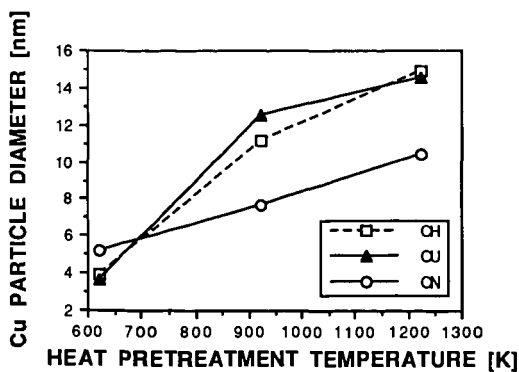


Figure 3. Variation in Average Cu Crystallite Diameter with Heat Pretreatment Temperature of Cu/Saran Catalysts.

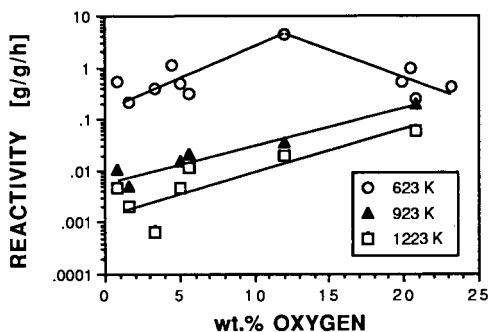


Figure 4. Effect of Carbon Surface Chemistry (% Initial Oxygen Content) on the Gasification Reactivity (at 623 K) of Cu/Saran Catalysts in 0.1 MPa Air, Following Heat Pretreatment at Different Temperatures (Indicated in the Figure).

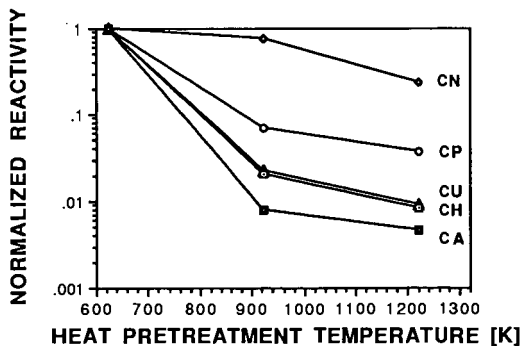


Figure 5. Normalized Loss in Gasification Reactivity (With Respect to Most Active Samples at 623 K) in 0.1 MPa Air for Cu/C Catalysts Differing in Chemical Pretreatment (see Table 1).

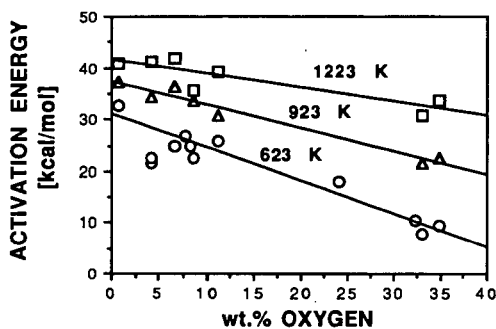


Figure 6. Effect of Carbon Surface Chemistry (% Initial Oxygen Content) on the Apparent Activation Energy of the Gasification Reaction of Cu/Saran Catalysts in 0.1 MPa Air, Following Heat Pretreatment at Different Temperatures (Indicated in the Figure).